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Thermodynamic properties of lanthanum in gallium–indium eutectic based alloys

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ABSTRACT

Activity and activity coefficients of lanthanum were determined for the first time in gallium–indium eutectic based alloys in a wide temperature range employing electromotive force method. Activity of β-La and super cooled liquid lanthanum in Ga–In eutectic based alloys between 573 and 1073 K linearly depends on the reciprocal temperature:

$$\lg a_{\beta\text{-La(Ga–In)}} = 5.660 - \frac{15,352}{T} \pm 0.093$$

$$\lg a_{\text{La(Ga–In)}} = 6.074 - \frac{15,839}{T} \pm 0.093$$

Activity coefficients of β-La and super cooled liquid lanthanum in this system at 617–1073 K are described by the following equations:

$$\lg \gamma_{\beta\text{-La(Ga–In)}} = 3.786 - \frac{12,216}{T} \pm 0.171$$

$$\lg \gamma_{\text{La(Ga–In)}} = 4.199 - \frac{12,703}{T} \pm 0.171$$

In addition activity of lanthanum in alloys with In was also determined in the same temperature range.

1. Introduction

Fast neutron reactors allow more efficient use of uranium resources. In addition this type of reactors is capable of burning long lived actinides (including those accumulated in thermal reactors spent fuel) thus reducing radioactivity of nuclear wastes. Application of fast reactors results in considerable increase of fuel burn up and, if the reactor is operated as breeder, reproduces fissile materials. At present non-aqueous pyrochemical methods employing molten salts and liquid metals are developed for reprocessing spent nuclear fuels (SNFs) of fast reactors. Inorganic melts have very high radiation stability and can be employed for organizing a short closed fuel cycle. Fissile elements and fission products dissolved in a salt melt can be separated employing selective extraction by liquid metals. Detailed information on the properties and behaviour of all elements present in SNF in fused salts and liquid metals is required to design a feasible separation process and these include rare earth elements representing an important group of fission products.

Thermodynamic estimates [1] show that from all low melting metals gallium is most efficient in separating lanthanides from uranium in a molten chloride salt – liquid metal system with separation coefficients of 10^4–10^5 at 800–1000 K. Uranium in this case remains in the fused salt phase and lanthanum in the metallic alloy. After extracting lanthanide fission products the metallic phase is then transferred to a repository for long term storage. Binary and ternary eutectic mixtures can be used to lower melting point of metallic alloys and thus the operation temperatures. Gallium–indium system offers one of the lowest melting eutectics with the melting point around 289 K [2], i.e., below ordinary room temperature. Liquids alloys based on the Ga–In eutectic can be safely transported and pumped without the need for the additional

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heating. Indium, being cheaper than gallium, also lowers the cost of the liquid alloy. Vapour pressure of the metallic phase is another important factor to consider. Vapour pressure above the metallic eutectic alloys can be estimated from the additivity rule and known temperature dependencies of vapour pressures of individual metals. For the Ga–In eutectic the vapour pressure is expected to be very low even at relatively high temperatures, e.g., at 1100 K estimates give the value around 8.66×10^{-5} mm Hg [3]. Thus the wide temperature range of the liquid state and low vapour pressures make Ga–In system very attractive for application in pyrochemical reprocessing of SNF. Lowering working temperatures simplifies technological process and construction of the apparatuses.

Selectivity of a pyrochemical separation process taking place at the molten salt – liquid metal interface depends on the properties of both phases. Knowing thermodynamic properties of all SNF components in working media is essential for determining applicability of a particular system for practical application. Behaviour of lanthanum has so far been studied only in binary systems, La–Ga and La–In [2,4–8]. There is no information on thermodynamic properties of lanthanum in ternary metallic alloys containing low melting metals and therefore it was of interest to assess the behaviour of a solute (lanthanum) in a mixed solvent (Ga–In) and to see how mixing two individual metal solvents affects the properties of a dissolved component. In the present study activity and activity coefficients of lanthanum were determined in the alloys based on Ga–In eutectic.

2. Experimental

The experiments were performed between 573 and 1073 K employing electromotive force (EMF) measurements. To determine lanthanum activity the EMF of the galvanic cell (1) were measured. In the cell the potentials of two-phase saturated alloys of lanthanum with Ga–In eutectic were measured relative to two-phase saturated La–In alloy. Application of metallic lanthanum as reference electrode is limited to *ca*. 900 K. At higher temperatures, especially at prolonged experiments, lanthanum can react with molten alkali chlorides displacing alkali metal. This problem can be solved by using lanthanum containing alloys instead of pure lanthanum and in the present study a two-phase saturated lanthanum-indium alloy (containing solid $LaIn_3$ intermetallic compound) was employed. Additional advantage of this reference electrode is the absence of phase transformations of $LaIn_3$ in the studied temperature range [3].

$$(-)\text{Liquid} + LaIn_3 \mid LiCl{-}KCl{-}CsCl + LaCl_3 \mid La{-}Ga{-}In(+) \qquad (1)$$

Activity coefficients of lanthanum were determined by measuring EMF of the cell (1) but this time with homogeneous La–Ga–In alloys with known La concentration. Difference between logarithms of activity (obtained from measured EMF values) and concentration (from the results of chemical analysis of the alloys) gave activity coefficients.To determine the potential difference between metallic lanthanum and two-phase La–In alloy the EMF of the following galvanic cell was measured:

$$(-)La \mid LiCl{-}KCl{-}CsCl + LaCl_3 \mid \text{Liquid} + LaIn_3(+) \qquad (2)$$

Ternary eutectic mixture of lithium, potassium and caesium chlorides was used as the solvent salt. This eutectic has low melting point of 536 K that allowed starting electrochemical measurements from as low as 573 K. LiCl–KCl–CsCl eutectic was prepared by fusing individual alkali chlorides mixed in the required proportion using the procedure described earlier [9]. Individual anhydrous salts (purity of 99.5% and above) used in the preparation of the eutectic were thoroughly dried under vacuum for several hours at temperatures exceeding the melting point by *ca*. 100 degrees, and then dry hydrogen chloride was bubbled through the molten salts to convert any oxide impurities to the chlorides. Lanthanum chloride containing melts were prepared by reacting lanthanum oxide with hydrogen chloride directly in the ternary eutectic melt. This procedure was preferred to direct dissolution of anhydrous $LaCl_3$ in the melt. Pure lanthanum trichloride can be prepared by standard procedures of chlorinating La_2O_3 but this hygroscopic compound should be kept and handled only under an inert atmosphere. In the present work lanthanum chloride containing melts were required and these can be easily prepared by chlorinating La_2O_3 directly in the fused salt. Previous studies showed that the reactions of lanthanide oxides with HCl in molten alkali chlorides goes to completion without any oxychlorides left in the melt [10,11]. Concentration of lanthanum in the melts used in the present study was 0.5–1.0 wt.%.

Gallium–indium eutectic alloy (21.8 wt.% In [2]) was obtained by fusing individual metals (Ga of 99.9999% purity and In of 99.9995%) in an inert (argon) atmosphere MBraun Unilab 1200/780 dry box. Lanthanum containing alloys containing over 0.8 wt.% La were prepared by adding required amount of metallic lanthanum to the Ga–In alloy. For lower lanthanum concentration the alloys were prepared by cathodic deposition of lanthanum from the chloride melt on Ga–In cathode directly in the experimental cell before commencing the EMF measurements. In this case a saturated La–In alloy acted as an anode.

Experimental cells schematically presented in Figs. 1 and 2 were used for the EMF measurements. Potentials of saturated La–In alloys *vs*. lanthanum were determined using the cell shown in Fig. 1. The cell was assembled in the inert atmosphere dry box. Sealed cell was then transferred into a vertical tube furnace and heated to 1020–1073 K. Beryllium oxide crucibles (1 and 9 in Fig. 1) were used to hold molten electrolyte and liquid metals. All measurements were conducted under argon atmosphere additionally purified by passing through zirconium turnings heated to 1073 K. Additional zirconium getter (17 in Fig. 1) was placed in alumina crucible at the bottom of the experimental cell.

After the cell reached desired temperature (measured by a thermocouple positioned in the molten salt electrolyte and protected by a BeO sheath) the electrochemical measurements began. The potential values were taken as stationary if they did not exhibit a tendency to a monotonous shift and did not change by more than 0.1–0.5 mV over an hour. From 2–4 h were required to reach the first stable potential readings. Tungsten wires and rods were used as current conductors to lanthanum and lanthanum containing alloys to exclude thermal EMF. EMF values were measured at zero current using an Autolab 302N potentiostat/galvanostat with GPES 4.9 software. After the potential value was recorded the temperature was lowered by *ca*. 50 degrees and the measurement repeated. After lowering temperature the potential stabilised after 0.5–1 h.

EMF between studied La–In–Ga alloys and the two-phase La–In alloy were measured using the cell shown in Fig. 2 in a way analogous to the described above. Several liquid alloy samples with various La content could be placed into one cell for simultaneous measurements. Two of these sample crucibles are shown in Fig. 2 as an example, but up to 20 were used in the actual experiments.

After the measurements were completed over the temperature interval desired the experimental cell was cooled and quenched salt melt dissolved in cold water. Lanthanum containing alloys were washed with water followed by ethanol and then dried at room temperature. To determine the alloys composition they were quantitatively dissolved in a mixture of nitric and hydrochloric acids and the resulting solutions analyzed by ICP-MS. Chemical analyses of the metallic alloys and quenched salt melt showed no appreciable changes in lanthanum concentration in comparison with the starting values (when La was added to the alloy by cathodic deposition initial lanthanum concentration was estimated from

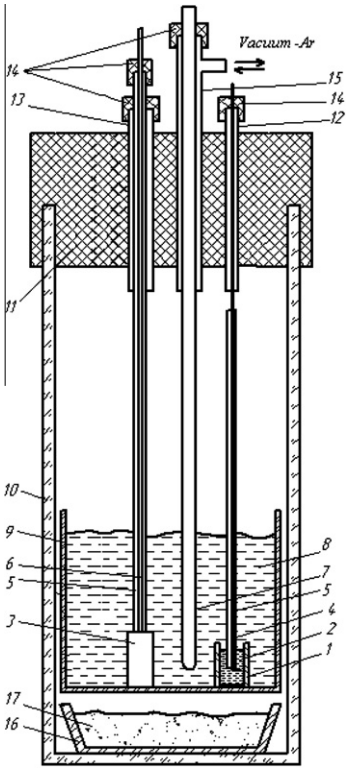

Fig. 1. Experimental cell. 1 – Small BeO crucible; 2 – liquid alloy; 3 – metallic La (reference electrode); 4, 6 – W wires; 5 – ceramic tube; 7 – BeO thermocouple sheath; 8 – electrolyte; 9 – large BeO crucible; 10 – silica cell; 11, 14 – rubber stoppers; 12, 13, 15 – silica tubes; 16 – alumina crucible; and 17 – Zr turnings (getter).

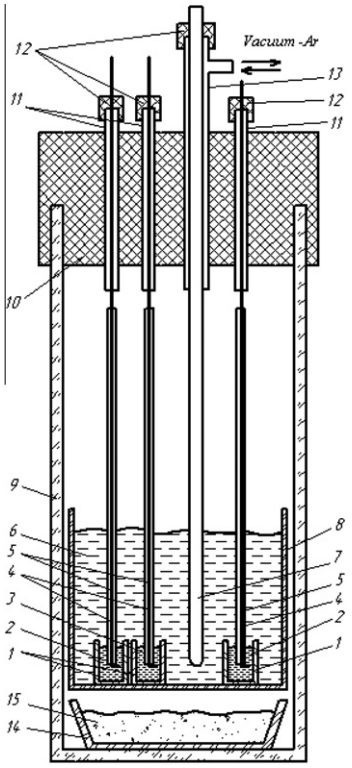

Fig. 2. Experimental cell. 1 – Small BeO crucible; 2 – liquid alloy; 3 – reference electrode (La–In + $LaIn_3$); 4 – ceramic tubes; 5 – W wires; 6 – electrolyte; 7 – BeO thermocouple sheath; 8 – BeO crucible; 9 – silica cell; 10, 12 – rubber stoppers; 11, 13 – silica tubes; 14 – alumina crucible; and 15 – Zr turnings (getter).

the quantity of the electricity passed). Thus even in prolonged experiments (with repeating measurements the experiments took up to 48 h) there was no redistribution of lanthanum between the salt and metallic phases.

3. Results and discussion

To calculate the potentials of La–Ga–In alloys relative to metallic lanthanum the EMF values of the galvanic cells (1) and (2) were added. Temperature dependence of EMF of the galvanic cell (2) is presented in Fig. 3. At 573–1073 K it can be approximated by Eq. (3) and is in a good agreement with the literature [5].

$$E = -2.37 \times 10^{-7} \cdot T^2 + 9.02 \times 10^{-5} \cdot T + 0.671 \pm 0.005\ \text{V} \qquad (3)$$

Activity of β-lanthanum in two-phase saturated La–In alloys containing $LaIn_3$ was calculated from the results of EMF measurements and the temperature dependence $\lg a_{La} = f(T)$ is presented in Fig. 4. The obtained results agree with the literature [5,7,8] and in the studied temperature range can be approximated by the following equation:

$$\lg a_{La(In)} = 4.297 - \frac{12,305}{T} \pm 0.104 \qquad (4)$$

When determining activity of lanthanum in Ga–In eutectic based alloys, β-lanthanum and super cooled liquid lanthanum were taken as standard states. To account for the phase transformations the following correction was added to the measured electrode potential values:

$$\Delta E = -\left(\frac{R \cdot T}{n \cdot F}\right) \cdot \ln a_0, \qquad (5)$$

where a_0 is lanthanum activity at working temperature relative to β-La or liquid lanthanum. The value of $\ln a_0$ was calculated from the known thermodynamic parameters of lanthanum phase transformations [12].

Temperature dependence of EMF of two-phase saturated alloys of lanthanum with Ga–In eutectic measured using the cell (1) and recalculated relative to β-La is shown in Fig. 5. At 573–1073 it is not linear and can be approximated by the following equation:

$$E = 1.42 \times 10^{-7} \cdot T^2 - 5.95 \times 10^{-4} \cdot T + 1.100 \pm 0.004\ \text{V} \qquad (6)$$

Non-linearity of Eq. (6) can be the consequence of a number of reasons. First, depending on temperature various intermetallic compounds, i.e., $LaGa_2$ and $LaGa_6$, can be present in equilibrium with the liquid alloy. Second, in a wide temperature range the alloys may not follow the Neumann–Kopp rule (the alloy's heat capacity does not equal to the additive sum of the components'

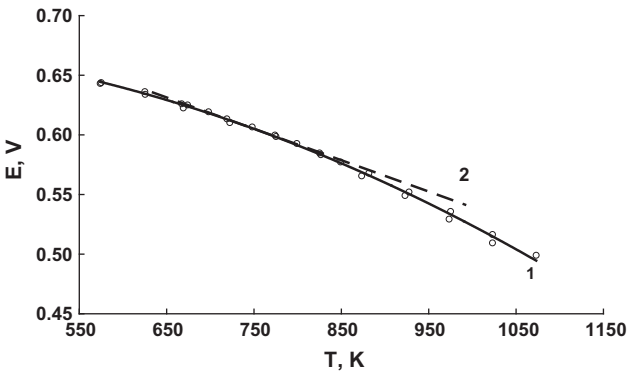

Fig. 3. The effect of temperature on EMF of La–In alloys saturated with lanthanum measured *vs.* lanthanum metal electrode: 1 – present work (9.8–10.4 wt.% La in the alloys) and 2 – [5].

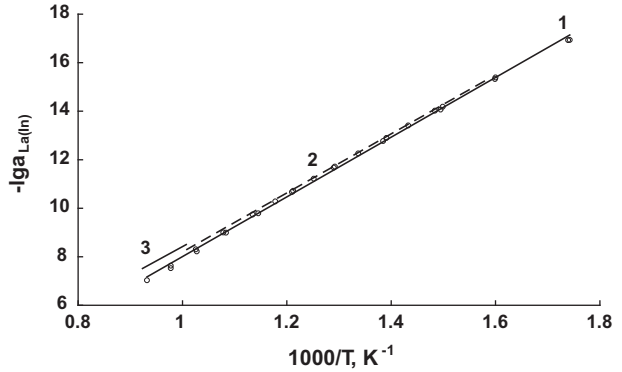

Fig. 4. Activity of β-lanthanum in La–In alloy saturated with lanthanum: 1 – present work, 2 – [5,7], and 3 – [8].

heat capacities). X-ray diffraction studies of the intermetallic phases precipitated from La–Ga–In alloys confirmed the formation of $LaGa_2$ and $LaGa_6$ phases.

Temperature dependence of β-La activity in two-phase La–Ga–In alloys is shown in Fig. 6 and it is very close to the results obtained by Kober et al. [5] for La–Ga alloys. At 573–1073 K the dependence $\lg a_{\beta\text{–La(Ga–In)}} = f(1/T)$ can be approximated by Eq. (7). Activity of super cooled liquid lanthanum is described by Eq. (8).

$$\lg a_{\beta\text{-La(Ga–In)}} = 5.660 - \frac{15,352}{T} \pm 0.093 \quad (7)$$

$$\lg a_{\text{La(Ga–In)}} = 6.074 - \frac{15,839}{T} \pm 0.093 \quad (8)$$

Activity coefficients of lanthanum were determined from the results of EMF measurements of the galvanic cell (1) containing homogeneous La–Ga–In alloys. Lanthanum concentration in the alloys varied from 0.1 to 6.5 wt.%, depending on temperature. The results obtained are shown in Fig. 7 where they are also compared with the literature data on La activity coefficients in La–Ga and La–In alloys. Again, as in the case with activity, activity coefficients of La in Ga–In based alloys are very close to γ_{La} in La–Ga alloys. At 617–1073 K activity coefficients of β-lanthanum and super cooled liquid lanthanum are expressed from the following equations:

$$\lg \gamma_{\beta\text{-La(Ga–In)}} = 3.786 - \frac{12,216}{T} \pm 0.171 \quad (9)$$

$$\lg \gamma_{\text{La(Ga–In)}} = 4.199 - \frac{12,703}{T} \pm 0.171 \quad (10)$$

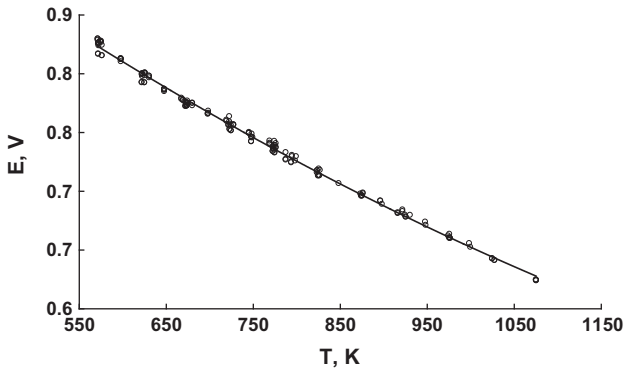

Fig. 5. Temperature dependence of EMF of saturated two-phase La–Ga–In alloys. Lanthanum concentration in the alloys varied from 0.2 to 18.7 wt.% depending on temperature.

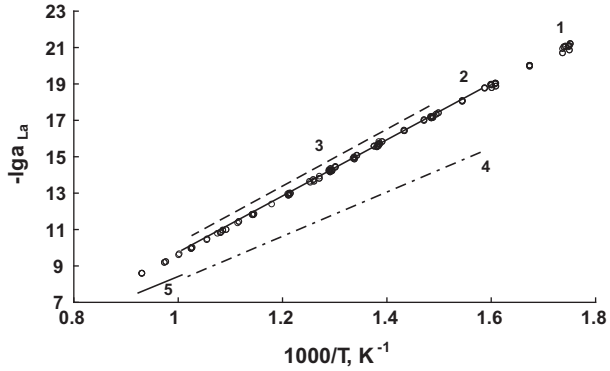

Fig. 6. The effect of temperature on activity of β-La in two-phase alloys with Ga, In and Ga–In eutectic: 1 – Ga–In, present work (symbols), 2 – Ga [5] (line), 3 – Ga [6]; 4 – In [5,7], and 5 – In [8].

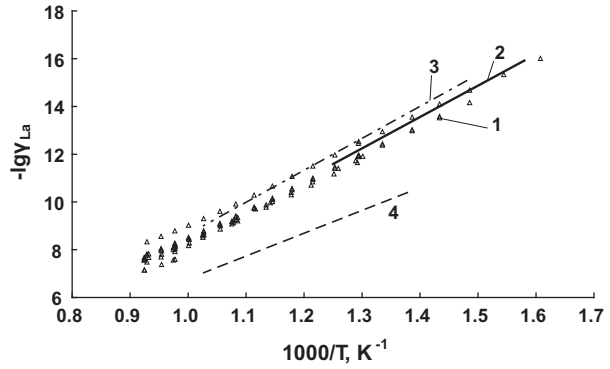

Fig. 7. The effect of temperature on activity coefficient of β-La in alloys with Ga, In and Ga–In eutectic: 1 – Ga–In present work (symbols); 2 – Ga [4,5]; 3 – Ga [6]; and 4 – In [7].

The results obtained in the present study show that activity and activity coefficients of lanthanum in alloys based on Ga–In eutectic within the limits of the experimental error closely correspond to the activity and activity coefficients of La in gallium alloys. This indicates that lanthanum in Ga–In alloys predominantly interacts with gallium. Indium acts as an additive merely lowering melting point of the alloy to 289 K and decreasing the cost of the low-melting metal phase. Low melting point of the alloys allows their safe transport by pumping at room temperature.

4. Conclusions

As a result of the present work activity and activity coefficients of lanthanum were determined for the first time in Ga–In eutectic based alloys. In two-phase alloys saturated with lanthanum two intermetallic compounds are present in the equilibrium with the liquid phase, i.e., $LaGa_6$ (below 750 K) and $LaGa_2$ (above 750 K). Activity of lanthanum was also determined in La–In alloys over a wider temperature range than previously given in the literature.

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